2009 fall

Advanced Physical Metallurgy

“Phase Equilibria in Materials”

09.15.2009

Eun Soo Park

Office: 33-316
Telephone: 880-7221
Email: espark@snu.ac.kr
Office hours: by an appointment

Contents for previous class

- Single component system

- **Gibbs Free Energy as a Function of Temp. & Pressure**

$$\boxed{G = H - TS}$$

$$\boxed{\left(\frac{\partial G}{\partial T}\right)_P = -S\,, \quad \left(\frac{\partial G}{\partial P}\right)_T = V\,, \quad \left[\frac{\partial(\frac{G}{T})}{\partial(\frac{1}{T})}\right]_P = H}$$

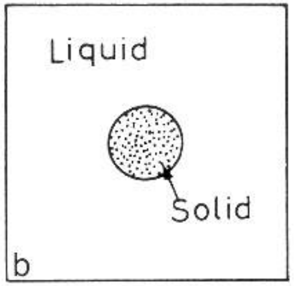
$$\boxed{\left(\frac{dP}{dT}\right)_{eq} = \frac{\Delta H}{T_{eq}\Delta V}}$$

Clausius-Clapeyron Relation :

(applies to all coexistence curves)

- **Driving force for solidification**

Liquid $\xrightarrow{\text{solidification}}$ Solid



$G_2 = G_1 + \Delta G$

$$\Delta G_r = -\frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \gamma_{SL}$$

$$\Delta G = \frac{L\Delta T}{T_m} = \frac{2\gamma_{SL}}{r^*}$$

Solid $\xrightarrow{\text{melting}}$ Liquid

$$\gamma_{SL} + \gamma_{LV} < \gamma_{SV}$$

In general, wetting angle = 0 ⇒ No superheating required!

Contents for today's class

CHAPTER 1 & 2

- Binary System
  - Gibbs Free Energy in Binary System

    Ideal solution and Regular solution

  - Chemical potential and Activity

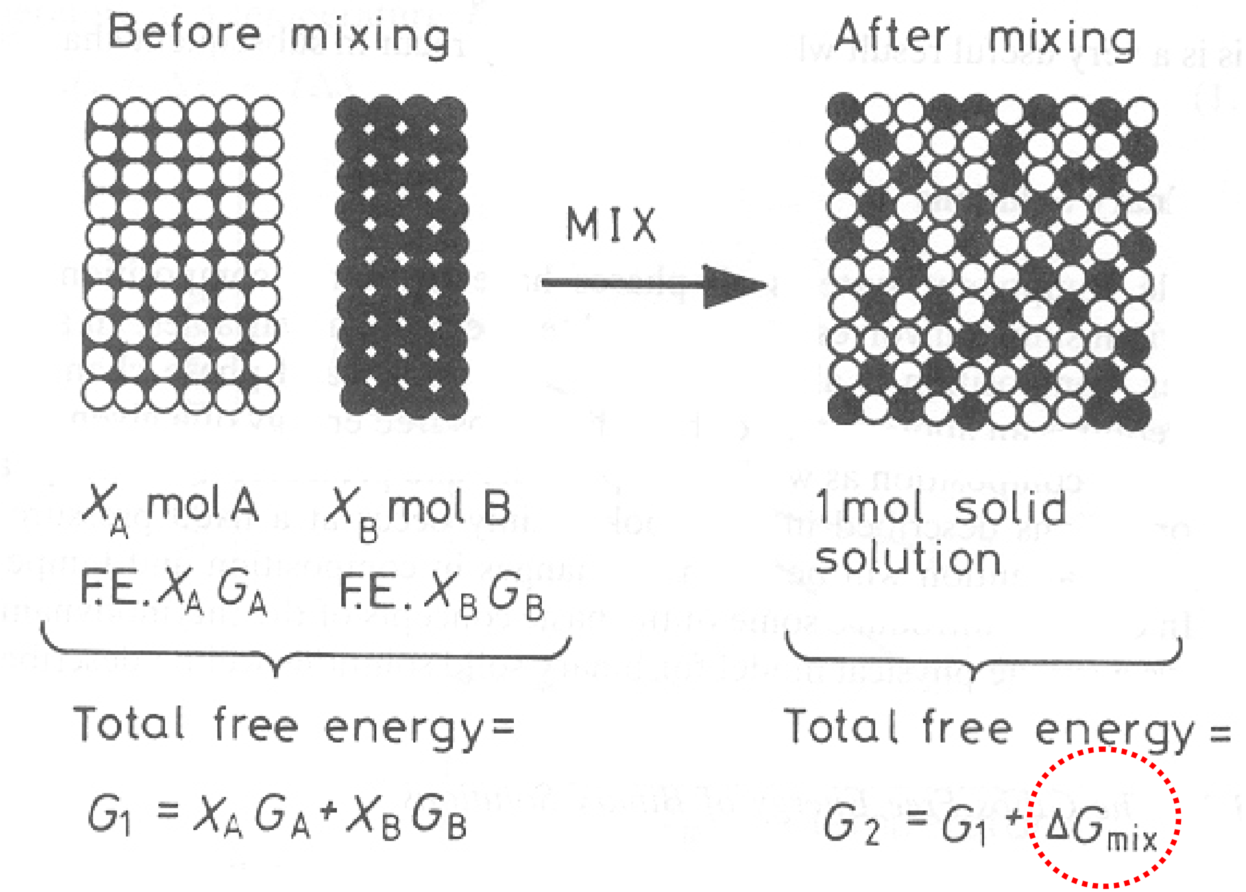
Binary Solutions: binary solid solution/ a fixed pressure of 1 atm

2) Gibbs Free Energy of Binary Solutions

*** Composition in mole fraction X_A, X_B $X_A + X_B = 1$**

1. bring together X_A mole of pure A and X_B mole of pure B

2. allow the A and B atoms to mix together to make a homogeneous solid solution.



$G_1 = X_A G_A + X_B G_B$

$G_2 = G_1 + \Delta G_{mix}$

Gibbs Free Energy of The System

In Step 1

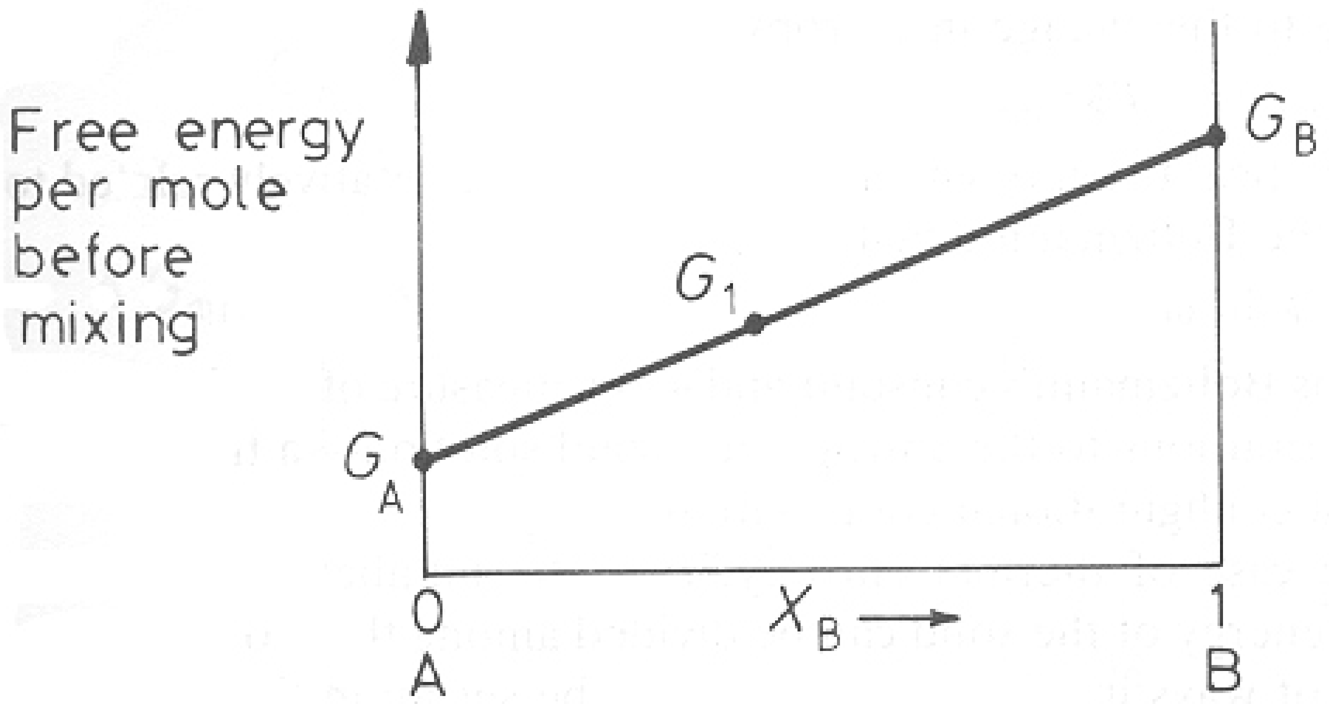
- **The molar free energies of pure A and pure B**

pure A; $G_A(T,P)$

pure B; $G_B(T,P)$

;X_A, X_B (mole fraction)

$$\boxed{G_1 = X_A G_A + X_B G_B \quad J/mol}$$

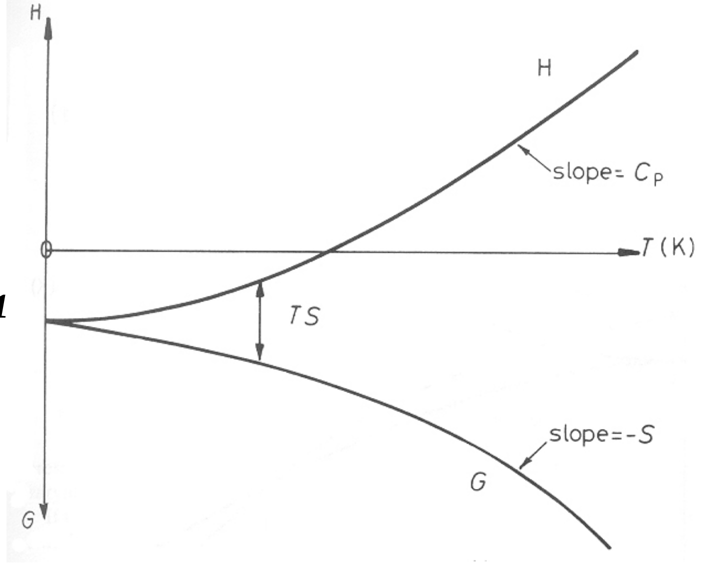


Free energy of mixture

Gibbs Free Energy of The System

In Step 2

$$\boxed{G_2 = G_1 + \Delta G_{mix} \quad J/mol}$$



Since $G_1 = H_1 - TS_1$ and $G_2 = H_2 - TS_2$

And putting $\Delta H_{mix} = H_2 - H_1$ $\Delta S_{mix} = S_2 - S_1$

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

ΔH_{mix} : ***Heat of Solution*** i.e. heat absorbed or evolved during step 2

ΔS_{mix} : ***difference in entropy*** between the mixed and unmixed state.

➡ ***How can you estimate ΔH_{mix} and ΔS_{mix} ?***

Mixing free energy ΔG_{mix}

- Ideal solution

Assumption; $\Delta H_{mix}=0$:

- **A& B_complete solid solution**
  (A,B ; same crystal structure)
- **no volume change** $H = E + \cancel{PV}$

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

$$\boxed{\Delta G_{mix} = -T\Delta S_{mix} \text{ J/mol}}$$

Entropy can be computed from randomness

by Boltzmann equation, i.e.,

$$\boxed{S = k \ln w}$$

w : degree of randomness, *k*: Boltzman constant

$$\boxed{S = S_{th} + S_{config}}$$

→ **thermal**; vibration (no volume change)

→ **Configuration**; the # of distinguishable ways of arranging the atoms

1) Ideal solution

Excess mixing Entropy

$$\Delta S^{mix} = -R(X_A \ln X_A + X_B \ln X_B)$$

$$\Delta G_{mix} = -T\Delta S_{mix} \Rightarrow \Delta G^{mix} = RT(X_A \ln X_A + X_B \ln X_B)$$

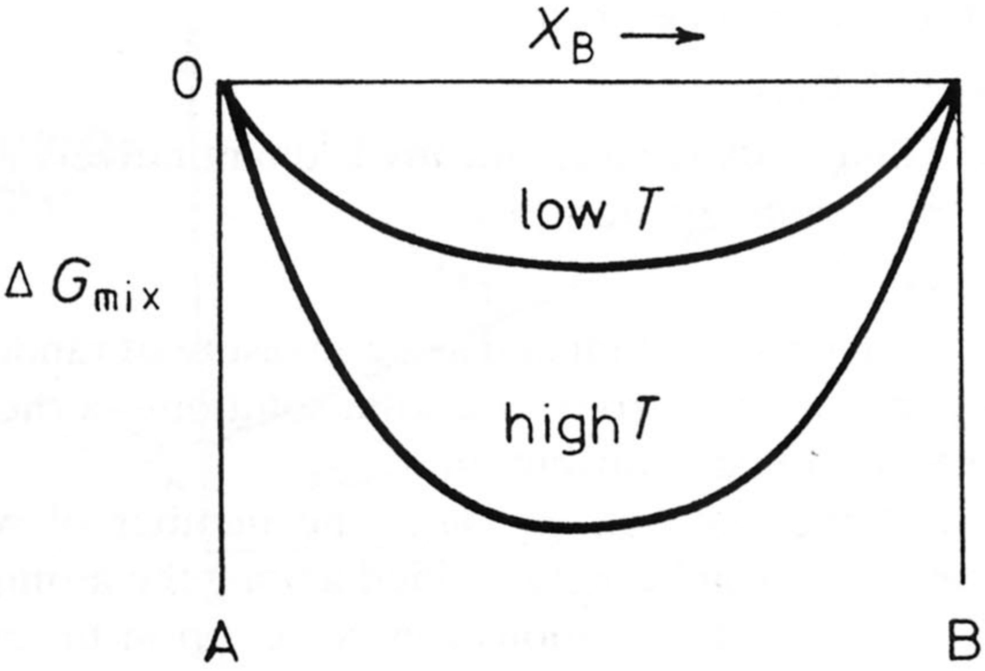


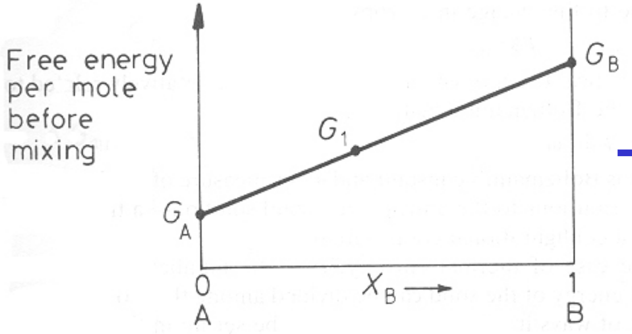
Fig. 1.9 Free energy of mixing for an ideal solution.

Since $\Delta H = 0$ for ideal solution,

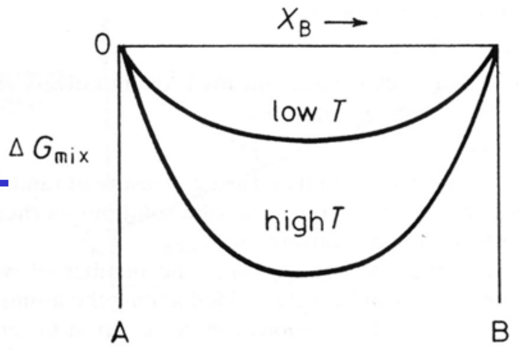
$$G_2 = G_1 + \Delta G_{mix}$$

$$\Rightarrow \quad G = X_A G_A + X_B G_B + RT(X_A \ln X_A + X_B \ln X_B)$$

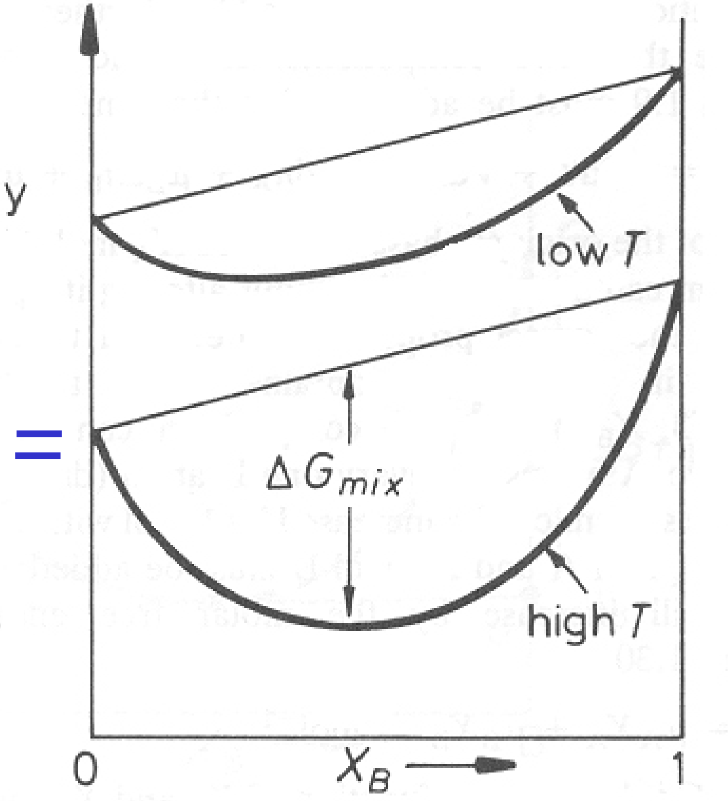
Compare $G_{solution}$ between high and low Temp.



+



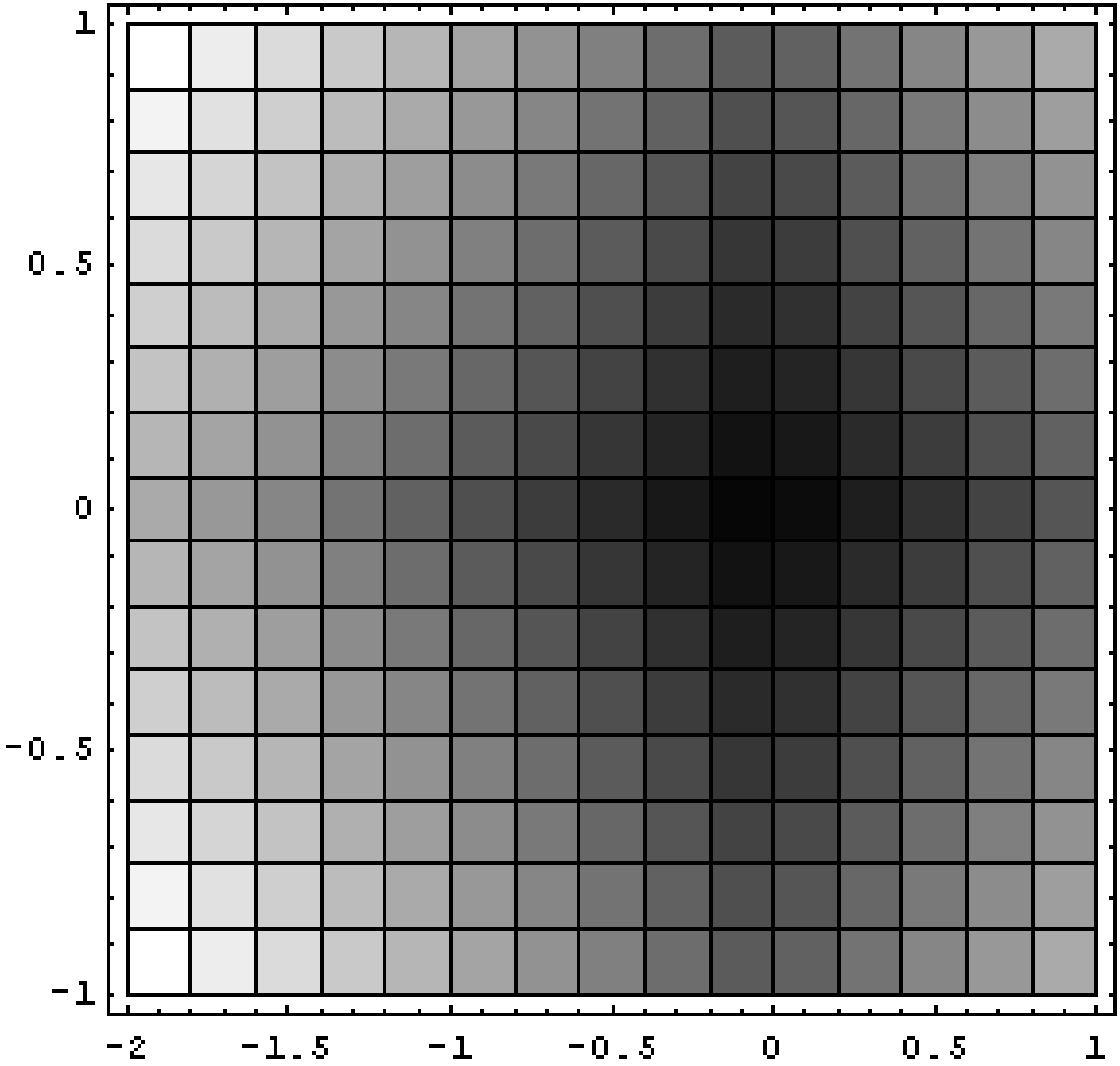
=



G_1

ΔG_{mix}

Fig. 1.10 The molar free energy (free energy per mole of solution) for an ideal solid solution. A combination of Figs. 1.8 and 1.9.


1
0.5
0
-0.5
-1
-2
-1.5
-1
-0.5
0
0.5
1

- Consider the chemical potential function over a hypothetical 2D region shown in the figure.
- Particles will tend to move from regions of high chemical potential (shown as lighter shades in plot) to regions of low chemical potential (shown as darker shades in plot). [particles: W → B]
- Various themodynamic properties determine what the chemical potential is.

For example, consider charged particles in a fluid.

- A concentration gradient in a fluid may promote movement of particles in one direction, and

-the electric potential gradient may promote movement of the particles in another.

-The chemical potential would account for both concentration and electric components and describe a potential distribution that determines net particle movement.

$G = H - TS = E + PV - TS$

1) Ideal solution

Chemical potential (Josiah Williard Gibbs)

Definition

If to any homogeneous mass in a state of hydrostatic stress we suppose an infinitesimal quantity of any substance to be added, the mass remaining homogeneous and its entropy and volume remaining unchanged, the increase of the energy of the mass divided by the quantity of the substance added is the *"potential"* for that substance in the mass considered.

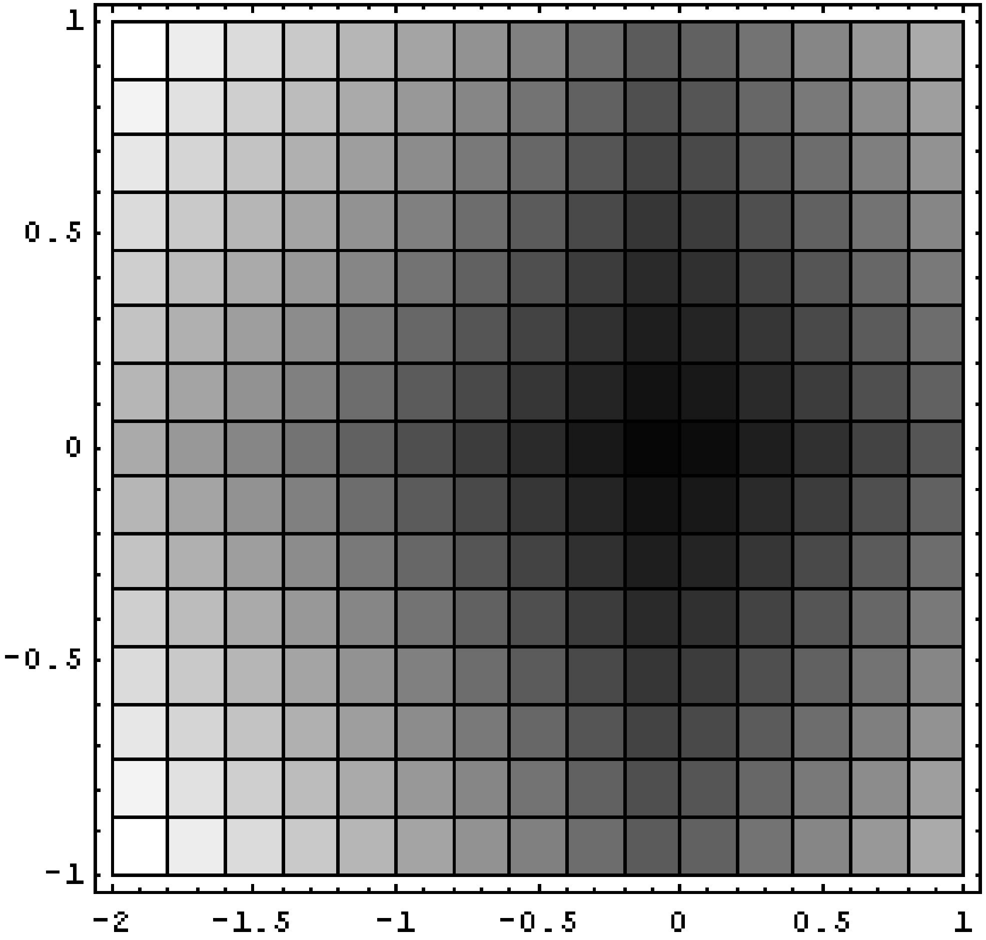
Gibbs noted also that for the purposes of this definition, any chemical element or combination of elements in given proportions may be considered a substance, whether capable or not of existing by itself as a homogeneous body. Chemical potential is also referred to as *"partial molar Gibbs energy".*

G = H-TS = E+PV-TS

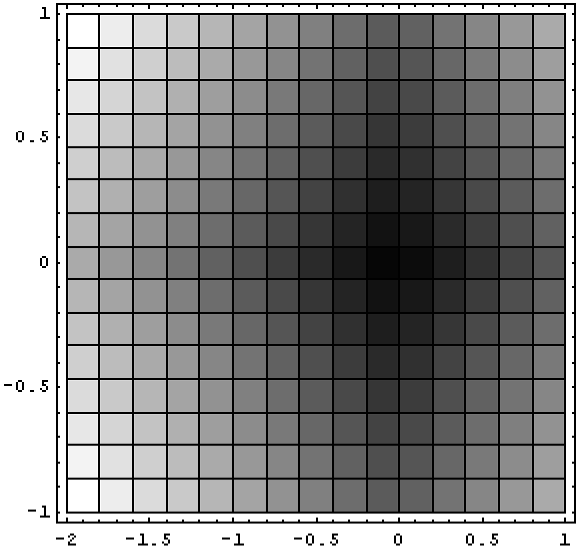
1) Ideal solution

Chemical potential

The increase of the total free energy of the system by the increase of very small quantity of A, dn_A, will be proportional to dn_A.



1) Ideal solution



$G = H\text{-}TS = E + PV\text{-}TS$

Chemical potential

The increase of the total free energy of the system by the increase of very small quantity of A, dn_A, will be proportional to dn_A.

$$\boxed{dG' = \mu_A dn_A}$$

(T, P, n_B: constant)

μ_A : **Chemical potential of A or partial morlar free energy of A**

$$\boxed{\mu_A = \left(\frac{\partial G'}{\partial n_A}\right)_{T,\,P,\,n_B}} \quad \boxed{\mu_B = \left(\frac{\partial G'}{\partial n_B}\right)_{T,\,P,\,n_A}}$$

For A-B binary solution, $dG' = \mu_A dn_A + \mu_B dn_B$

For variable T and P

$$dG' = -SdT + VdP + \mu_A dn_A + \mu_B dn_B$$

Correlation between chemical potential and free energy

For 1 mole of the solution (T, P: constant)

$$G = \mu_A X_A + \mu_B X_B \quad \mathrm{Jmol^{-1}}$$

$$dG = \mu_A dX_A + \mu_B dX_B$$

$$\frac{dG}{dX_B} = \mu_B - \mu_A$$

$$\mu_A = \mu_B - \frac{dG}{dX_B}$$

$$G = \left(\mu_B - \frac{dG}{dX_B}\right) X_A + \mu_B X_B$$

$$= \mu_B X_A - \frac{dG}{dX_B} X_A + \mu_B X_B$$

$$= \mu_B - \frac{dG}{dX_B} X_A$$

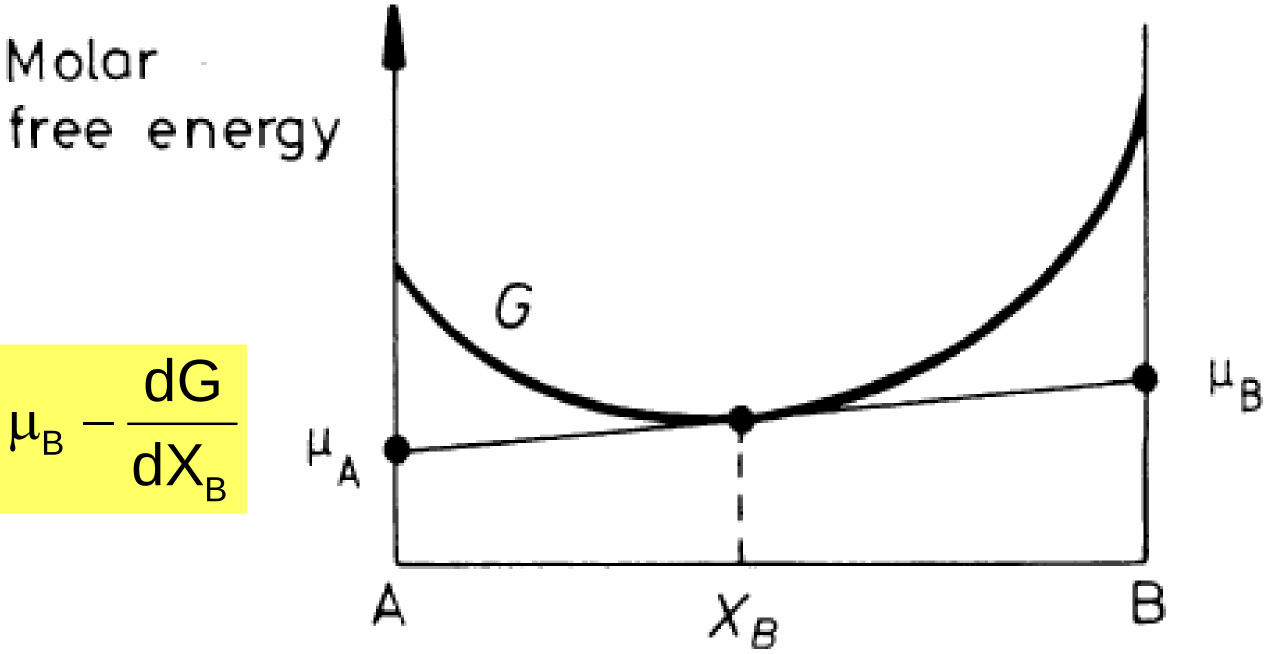
$$= \mu_B - \frac{dG}{dX_B}(1 - X_B)$$

$$\mu_B = G + \frac{dG}{dX_B} X_A$$

Correlation between chemical potential and free energy

For 1 mole of the solution (T, P: constant)

$$G = \mu_A X_A + \mu_B X_B \quad \mathrm{J\,mol^{-1}}$$



$$\mu_A = \mu_B - \frac{dG}{dX_B}$$

$$\mu_B = G + \frac{dG}{dX_B} X_A$$

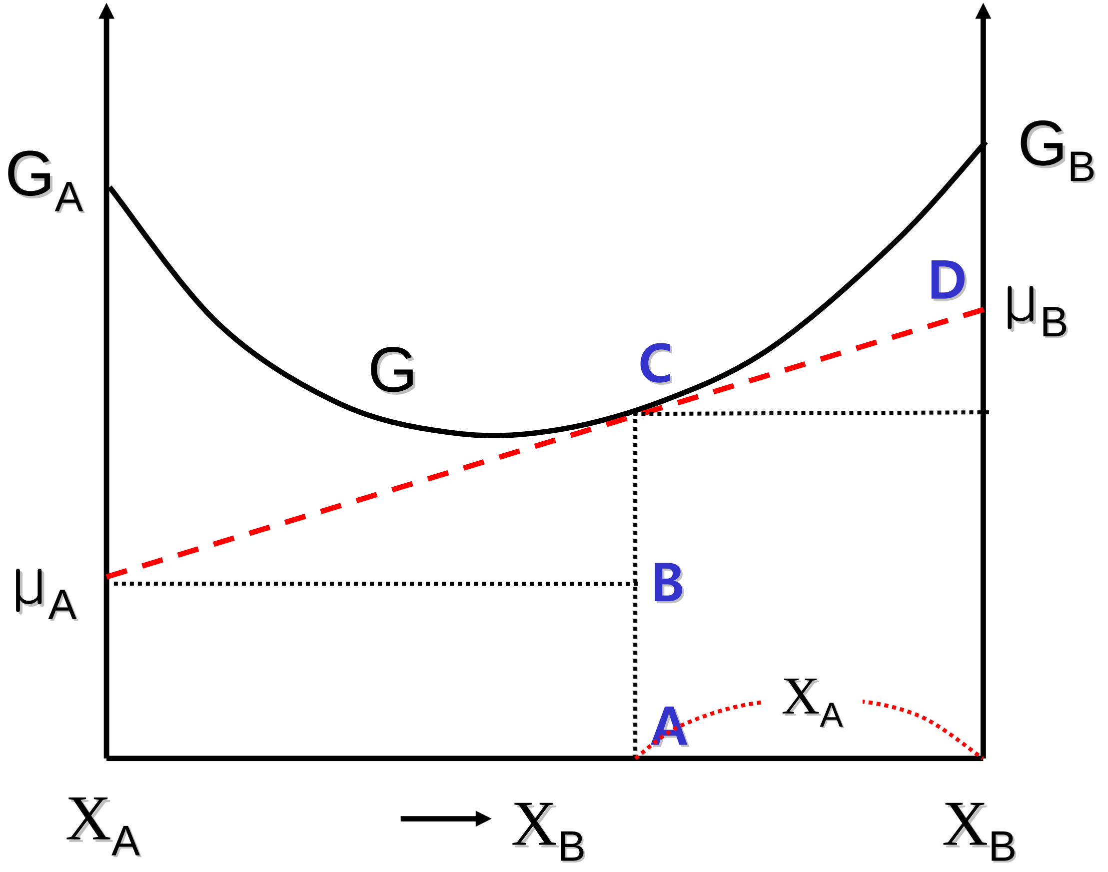
Fig. 1.11 The relationship between the free energy curve for a solution and the chemical potentials of the components.

Correlation between chemical potential and free energy

For 1 mole of the solution (T, P: constant)

1) Ideal solution

$$G = \mu_A X_A + \mu_B X_B \quad \text{Jmol}^{-1}$$



$$\mu_B = G + \frac{dG}{dX_B} X_A$$

$$\mu_B = G + \frac{dG}{dX_B}(1 - X_B)$$

$$\mu_A = \mu_B - \frac{dG}{dX_B}$$

$$= \mu_B - (X_A + X_B)\frac{dG}{dX_B}$$

$$= \overline{DA} - \overline{DC} - \overline{CB}$$

Chemical potential

1) Ideal solution

$$G = X_A G_A + X_B G_B + RT(X_A \ln X_A + X_B \ln X_B)$$

$$= (G_A + RT \ln X_A)X_A + (G_B + RT \ln X_B)X_B$$

$$\mu_A = G_A + RT \ln X_A$$

$$\mu_B = G_B + RT \ln X_B$$

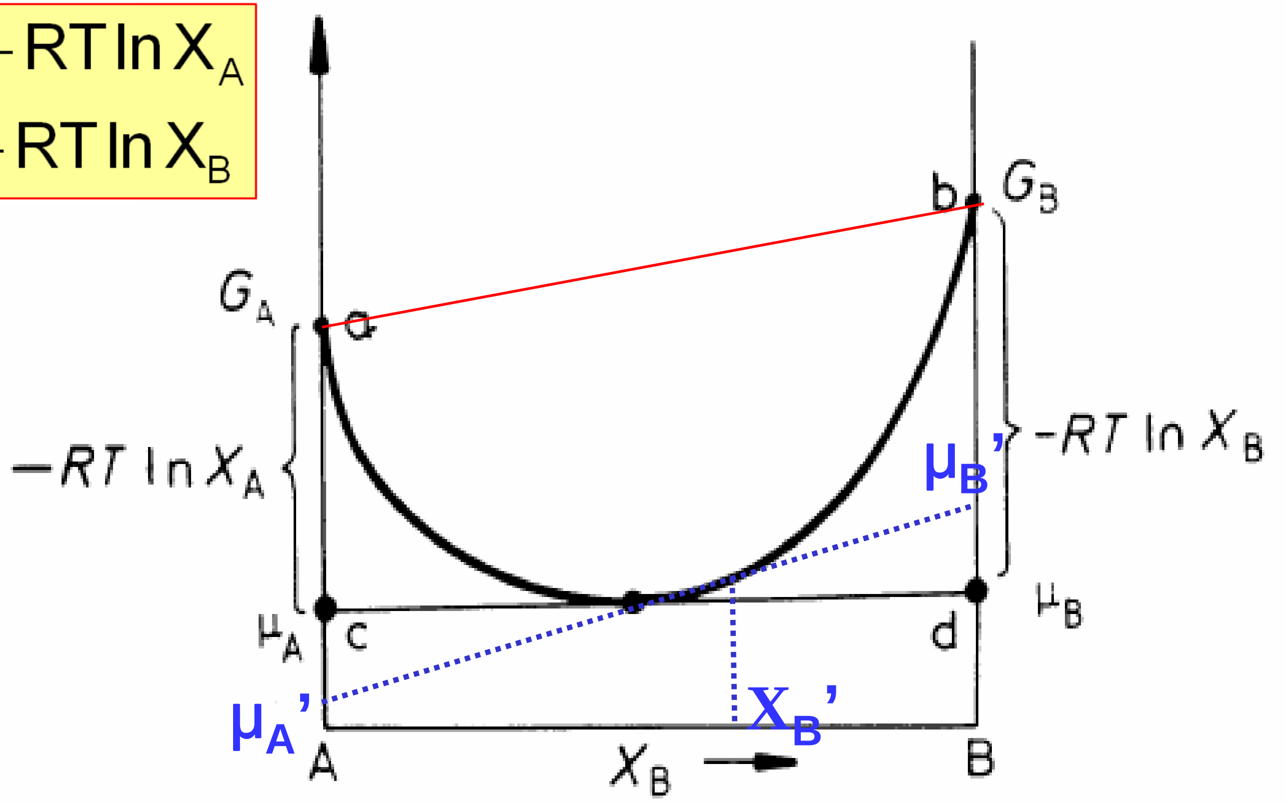


Fig. 1.12 The relationship between the free energy curve and chemical potentials for an ideal solution.

Regular Solutions

Ideal solution : $\Delta H_{mix} = 0$ $\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$

Quasi-chemical model assumes that heat of mixing, ΔH_{mix}, is only due to the bond energies between adjacent atoms.

Structure model of a binary solution

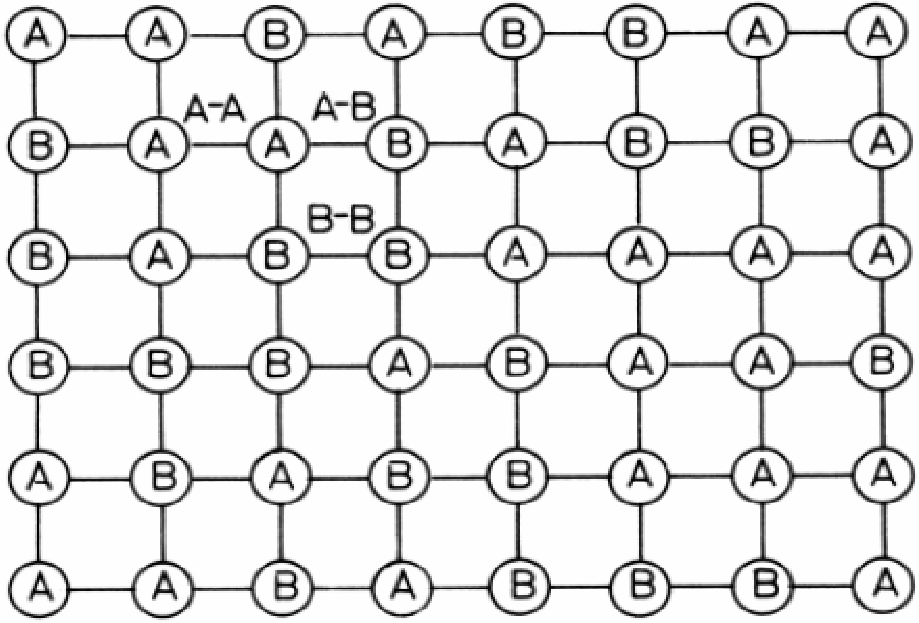


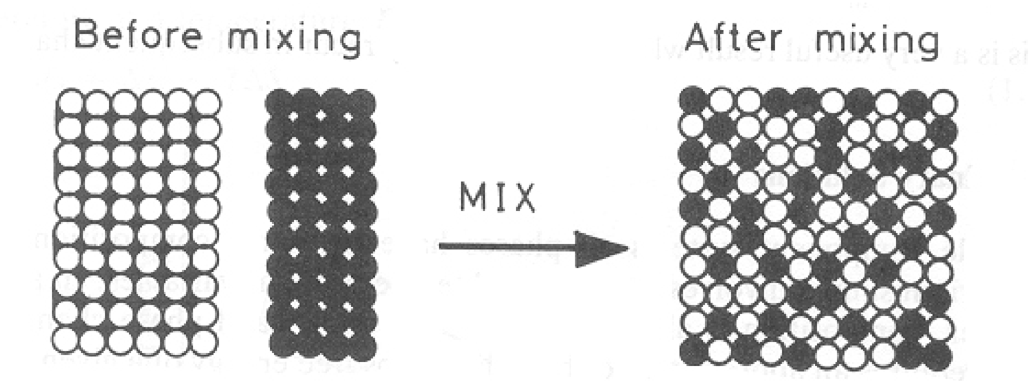
Fig. 1.13 The different types of interatomic bond in a solid solution.

Regular Solutions

	Bond energy	Number of bond
A-A	ε_{AA}	P_{AA}
B-B	ε_{BB}	P_{BB}
A-B	ε_{AB}	P_{AB}

Internal energy of the solution

$$E = P_{AA}\varepsilon_{AA} + P_{BB}\varepsilon_{BB} + P_{AB}\varepsilon_{AB}$$



$$\boxed{\Delta H_{mix} = P_{AB}\varepsilon}$$ where $\varepsilon = \varepsilon_{AB} - \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})$

Regular Solutions

Completely random arrangement

$$\varepsilon = 0 \quad \Rightarrow \quad \varepsilon_{AB} = \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})$$

$\Delta H_{mix} = 0$ ideal solution

$\underline{P_{AB} = N_a z X_A X_B}$ bonds per mole

N_a : Avogadro's number

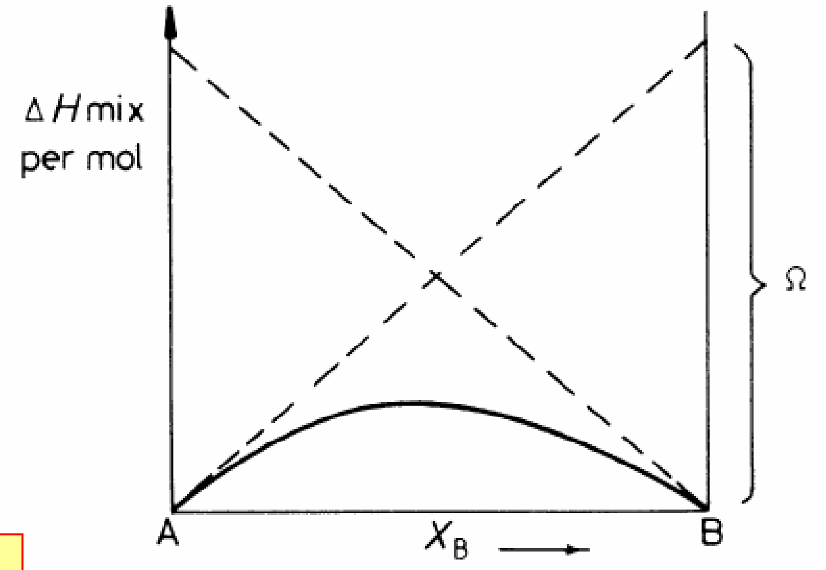
z : number of bonds per atom

$\varepsilon < 0 \rightarrow P_{AB} \uparrow$ $\varepsilon > 0 \rightarrow P_{AB} \downarrow$

$\boxed{\varepsilon \approx 0}$ ⇒ $\Delta H_{mix} = P_{AB}\varepsilon$

$$\boxed{\Delta H_{mix} = \Omega X_A X_B \quad \text{where} \quad \Omega = N_a z \varepsilon}$$

Regular Solutions



Ω >0 인 경우

Fig. 1.14 The variation of ΔH_{mix} with composition for a regular solution.